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Anchoring the Gas-Phase Acidity Scale[†]

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Theoretical calculations and experimental values from the recent literature are used to construct and evaluate a high precision gas-phase acidity scale. Gas-phase acidities at 0 K are evaluated for 12 reference species with accurately known acidities. Using recent spectroscopic results, small but significant revisions are presented for the acidities of ammonia, water, and formaldehyde. These revised anchor acidities are applied to previous thermokinetic or equilibrium measurements of the acidities of small alkanols, ethene, and benzene. Combined with electron affinities from literature negative ion photoelectron spectroscopy measurements, the revised acidities yield the following improved bond dissociation enthalpies: $D_{298}(CH_3O-H) = 437.7 \pm 2.8$ kJ/mol, $D_{298}(C_2H_5O-H) = 438.1 \pm 3.3$ kJ/mol, $D_{298}((CH_3)_2CHO-H) = 442.3 \pm 2.8$ kJ/mol, $D_{298}((CH_3)_3CO-H) = 444.9 \pm 2.8$ kJ/mol, $D_{298}(C_2H_3-H) = 463.0 \pm 2.7$ kJ/mol, and $D_{298}(C_6H_5BH) = 472.2 \pm 2.2$ kJ/mol. Calculation of gas-phase acidities at 0 K are investigated for several levels of theory. Excellent performance at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level is found for 16 acids composed of elements through chlorine, with a mean error of −0.2 kJ/mol and a mean absolute error of 1.5 kJ/mol.

Introduction

The negative ion thermochemistry cycle, eq 1 and Figure 1, relates the bond dissociation energy of a neutral molecule with its gas-phase acidity (deprotonation enthalpy) and the electron affinity of the radical.

$$D(\mathrm{HA}) = \Delta_{\mathrm{acid}}H(\mathrm{HA}) + \mathrm{EA}(\mathrm{A}) - \mathrm{IE}(\mathrm{H}) \qquad (1)$$

This relationship has been used extensively to obtain bond dissociation energies from spectroscopic, kinetic, and equilibrium experiments on the A^- anions.[1,2] Accurate electron affinities for hundreds of radical species are available from negative ion photodetachment spectroscopy, with accuracies of 3−10 meV or 0.3−1 kJ/mol, or better for atoms and some small molecules.[3−5] An extensive gas-phase acidity scale also including hundreds of molecules has been constructed from gas-phase ion−molecule equilibrium experiments.[6,7] Proton-transfer equilibrium measurements provide the differences between the Gibbs energies of deprotonation of two acids, eq 2:

$$\mathrm{A}^- + \mathrm{HB} \rightleftharpoons \mathrm{HA} + \mathrm{B}^-$$
$$\Delta_r G = \Delta_{\mathrm{acid}}G(\mathrm{HB}) - \Delta_{\mathrm{acid}}G(\mathrm{HA}) \qquad (2)$$

Individual equilibrium experiments can be precise, giving $\Delta_r G$ within 1 kJ/mol, but obtaining an absolute gas-phase acidity requires a known value for one of the acids. Because equilibrium measurements are usually practical only between two molecules with acidities within 10−20 kJ/mol of each other, most acids have not been measured directly against a well-known reference acid. Uncertainties in anchoring the gas-phase acidity scale typically limit the accuracy of acidities to ±8 kJ/mol.[6,7]

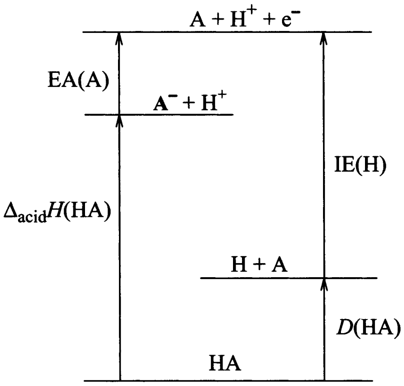

Figure 1. Schematic energy diagram showing the negative ion thermochemistry cycle, eq 1.

We have recently developed an alternative thermokinetic method for measuring relative gas-phase acidities.[8,9] It employs energy-resolved, competitive collision-induced dissociation measurements,[10] on a proton-bound anionic heterodimer, eq 3, where xenon is an inert target gas:

$$[\mathrm{A}\cdot\cdot\mathrm{H}\cdot\cdot\mathrm{B}]^- + \mathrm{Xe} \rightarrow \mathrm{A}^- + \mathrm{HB} + \mathrm{Xe}\ E_0(1)$$
$$\rightarrow \mathrm{HA} + \mathrm{B}^- + \mathrm{Xe}\ E_0(2) \qquad (3)$$

The product branching ratio as a function of excess energy above the threshold is modeled using RRKM statistical rate theory[8,10,11] to obtain the relative threshold energy difference, $\Delta E_0 = E_0(2) - E_0(1) = \Delta_{\mathrm{acid}}H_0(\mathrm{HB}) - \Delta_{\mathrm{acid}}H_0(\mathrm{HA})$, within ±3 to ±5 kJ/mol. That is less precise than equilibrium measurements, but the two acidities can differ by up to 50 kJ/mol, more often allowing measurement of the unknown directly against a well-known reference acid. The modeling of the reaction thresholds

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TABLE 1: Selected Dissociation Energies, Electron Affinities, and Gas-Phase Acidities

HA	D_0(H−A)/ kJ mol^{-1}	ref	D_{298}(H−A)^a/ kJ mol^{-1}	EA$_0$(A)/eV	ref	$\Delta_{acid}H_0$(HA)/ kJ mol^{-1}	ref
CH_4	432.71 ± 0.13	18	439.28 ± 0.13	0.080 ± 0.030	29	1737.0 ± 2.9	eq 1
NH_3	443.99 ± 0.24	31	450.08 ± 0.24	0.771 ± 0.005	30	1681.7 ± 0.5	eq 1
H_2	432.071 ± 0.012	23,34	435.996 ± 0.012	0.754203754 ± 0.000000060	5	1671.360 ± 0.012	22
H_2CO	362.809 ± 0.006	37	368.795 ± 0.032	0.313 ± 0.005	39	1644.7 ± 0.5	eq 1
H_2O	492.28 ± 0.06	26	497.38 ± 0.06	1.827653 ± 0.000004	40	1627.98 ± 0.06	eq 1
HCCH	551.2 ± 0.1	49	557.8 ± 0.3	2.969 ± 0.006	50	1576.8 ± 0.6	eq 1
HF	565.97 ± 0.06	52	570.09 ± 0.06	3.4011887 ± 0.0000031	53,54	1549.854 ± 0.012	55
H_2S	376.1 ± 0.5	57	381.4 ± 0.5	2.314338 ± 0.000025	59	1464.92 ± 0.04	21
HCN	522.9 ± 0.8	61	528.5 ± 0.8	3.862 ± 0.004	60	1462.3 ± 0.9	eq 1
HCl	427.78 ± 0.10	23,34	431.61 ± 0.10	3.61272 ± 0.00003	63	1391.122 ± 0.007^b	20
HBr	362.41 ± 0.20	23,34	366.16 ± 0.20	3.3635880 ± 0.0000019	53	1349.92 ± 0.20	eq 1
HI	294.52 ± 0.12	23,34	298.26 ± 0.12	3.059036 ± 0.000010	64	1311.42 ± 0.12	eq 1

[a] Dissociation ethalpy at 298 K from same reference as at 0 K, if reported; otherwise, thermal corrections are given in the Supporting Information. [b] For H^{35}Cl.

yields the gas-phase acidity difference at 0 K. We have been motivated by these experiments to develop a gas-phase acidity scale of $\Delta_{acid}H_0$ values. This work evaluates the acidities of 12 selected anchor species at 0 K, compares these with the equilibrium acidity scale of $\Delta_{acid}G_{298}$ values, and applies the results to revise previously reported acidities and dissociation energies of small alkanols,[8] ethene,[12] and benzene.[13]

This work further examines the performance of ab initio calculations of gas-phase acidities at various levels of theory and uses the results to check the reliability of the experimental acidities. Theoretical calculations of energetics are becoming increasingly accurate. Discrepancies between experimental and theoretical energies, especially for first- and second-row species, are now cause for concern that either the experiment or theory is subject to specific errors or artifacts. The calculation of gas-phase acidities for comparison to experimental results, rather than either neutral bond dissociation energies or electron affinities, has several advantages. For the acids considered here, HA and A$^-$ are both closed-shell singlets and have the same number of electrons, whereas the neutral radicals A are doublets and subject to spin-contamination issues. Low-lying electronic excited states are not present in HA and A$^-$ but may be in A. Errors that are proportional to the number of electrons cancel in the calculation of the gas-phase acidity, $\Delta_{acid}H_0 = E(A^-) - E(HA)$. Indeed, the empirical corrections for “higher-level” effects and the spin−orbit corrections in Gaussian-3 theory[14] are exactly zero for gas-phase acidities. Here, we compare standard model thermochemistry methods (Gaussian-3[14] and complete basis set[15] models), density functional theory, and coupled-clustered theory for gas-phase acidity calculations.

Evaluation of Experimental Acidities at 0 K for Benchmark Reference Acids

Accurate acidities for reference acids have typically been obtained by eq 1 from high-resolution spectroscopic or calorimetric measurements of the bond dissociation energy combined with the electron affinity of the radical from photodetachment spectroscopy.[1] Photofragment translational spectroscopy (PTS) experiments,[16] in which the kinetic energy spectrum of a photodissociation product is measured with resolution of the rovibronic states of reactant and products, provide some of the most precise direct measurements of bond dissociation energies. High-quality dissociation energies are also obtained from photoionization threshold energies via the positive ion thermochemical cycle, eq 4,

$$D_0(H-A) = AE_0(A^+,HA) - IE_0(A) \qquad (4)$$

which derives the dissociation energy from the appearance energy of a fragment ion in dissociative ionization and the ionization energy of the fragment.[17−19] A method for direct spectroscopic measurement of the ion-pair formation threshold energies for the process HA → H$^+$ + A$^-$ has recently been developed by Hepburn and co-workers.[20−22] These threshold ion-pair production spectroscopy (TIPPS) experiments are similar in concept to zero-electron-kinetic-energy photoelectron spectroscopy (ZEKE-PES). TIPPS experiments yield acidities with the extraordinary precision of within 1−3 cm^{-1} (0.01−0.03 kJ/mol) for small molecules. In our evaluation of acidities, the direct high-precision TIPPS determinations of the ion-pair formation energies are preferred. The second choice is acidities calculated from experimental bond dissociation energies and electron affinities via the negative ion thermochemical cycle, eq 1. Our recommendations for electron affinities mostly follow recent reviews of atomic[5] and molecular[4] electron affinities.

The species H_2, H_2O, HF, H_2S, HCl, HBr, and HI can be considered as primary anchors or benchmarks because their acidities are believed to be known to within 0.5 kJ/mol and because the thermodynamic functions of HX and X$^-$ as a function of temperature have been evaluated.[23,24] Experimental values are always subject to reexamination, of course, as illustrated by the recent revision[19,25,26] in the dissociation energy of water by 2 kJ/mol, an amount 10 times greater than the previous accepted uncertainty (discussed further below). As secondary anchors, we also include CH_4, NH_3, H_2CO, HCCH, and HCN, whose acidities are known to within 1−3 kJ/mol using eq 1.

The evaluated acidities, bond dissociation energies, and electron affinities at 0 K are listed in Table 1 and discussed below in order of increasing acid strength (decreasing magnitude of $\Delta_{acid}H$). Table 1 also includes bond dissociation enthalpies at 298 K, D_{298}(R−H). Literature values are given in the units reported, then converted using 1 cal = 4.184 J, 1 cm^{-1} = 0.01196265649 ± (1.8 × 10^{-10}) kJ/mol (hcN_A), or 1 eV = 96.485341 ± 0.000017 kJ/mol (eN_A) = 8065.54477 ± 0.00064 cm^{-1} (e/hc) from the 1998 CODATA recommendations.[27] The ionization energy of atomic hydrogen[23] is IE$_0$(H) = 109678.764 ± 0.001 cm^{-1} = 1312.04938 ± 0.00002 kJ/mol. The reported uncertainties are those of the original authors. If the confidence interval is specified in the original reference, we have converted to ±2 standard uncertainties[28] or about the 95% confidence level.

Methane. A precise value for the bond dissociation energy of methane comes from photoionization threshold measurements in a thermochemical network of related values,[18] $D_0(CH_3-H)$ = 103.42 ± 0.03 kcal/mol = 432.71 ± 0.13 kJ/mol. The electron affinity of the methyl radical from negative ion photoelectron spectroscopy[29] is $EA_0(CH_3) = 0.080 \pm 0.030$ eV $= 7.7 \pm 2.9$ kJ/mol. Using eq 1, the resulting gas-phase acidity of methane is $\Delta_{acid}H_0(CH_4) = 1737.0 \pm 2.9$ kJ/mol.

Ammonia. The electron affinity of NH_2 from photoelectron spectroscopy[30] of NH_2^- is $EA_0(NH_2) = 0.771 \pm 0.005$ eV $=$ 74.4 ± 0.5 kJ/mol. The bond dissociation energy of ammonia from PTS experiments[31] is $D_0(NH_2{-}H) = 37115 \pm 20$ cm^{-1} $= 443.99 \pm 0.24$ kJ/mol. The positive ion cycle (eq 4) gives a larger dissociation energy,[1,32] $D_0(NH_2{-}H) = AE_0(NH_2{+},NH_3) - IE_0(NH_2) = 106.7 \pm 0.3$ kcal/mol $= 446.4 \pm 1.3$ kJ/mol. Song et al.[33] argue (citing a personal communication from Berkowitz) that a slightly higher NH_2 ionization energy and thus a lower dissociation energy is consistent with the observed photoionization threshold[32] for NH_2, which has a weak Franck–Condon transition strength and an autoionization resonance near the onset. We also adopt the higher-precision PTS dissociation energy, which together with the electron affinity gives $\Delta_{acid}H_0(NH_3) = 1681.7 \pm 0.5$ kJ/mol.

Hydrogen. The bond dissociation energy of hydrogen is well established,[23,34] $D_0(H_2) = 432.071 \pm 0.012$ kJ/mol. From photodetachment threshold experiments,[35] $EA_0(H) = 6082.99 \pm 0.15$ cm^{-1} $= 72.7687 \pm 0.0018$ kJ/mol, but a theoretical value is considered more accurate,[5] $EA_0(H) = 6083.064145 \pm 0.000030$ cm^{-1} $= 72.7696068 \pm 0.0000012$ kJ/mol. Using these values in eq 1 yields $\Delta_{acid}H_0(H_2) = 1671.351 \pm 0.012$ kJ/mol. Recent TIPPS experiments[22] on the process $H_2 \rightarrow H^+ + H^-$ give a direct measurement of $\Delta_{acid}H_0(H_2) = 139714.8 \pm 1.0$ cm^{-1} $= 1671.360 \pm 0.012$ kJ/mol, in complete agreement with the negative ion thermochemical cycle.

Formaldehyde. The rovibronically resolved photodissociation threshold energy of formaldehyde from Moore and co-workers[36] yields $D_0(H{-}HCO) = 86.57 \pm 0.16$ kcal/mol $= 362.2 \pm 0.7$ kJ/mol. Using similar experiments at higher resolution, Terentis and Kable[37] find $D_0(H{-}HCO) = 30328.5 \pm 0.5$ cm^{-1} $= 362.809 \pm 0.006$ kJ/mol. Kinetic studies[38] of the hydrogen abstraction reactions of the CHO radical with HI and HBr yield $D_{298}(H{-}HCO) = 370.86 \pm 0.56$ kJ/mol. Correcting to 0 K using integrated heat capacities from Gurvich et al.[23,24] gives $D_0(H{-}HCO) = 364.87 \pm 0.56$ kJ/mol, which is 2.1 kJ/mol higher than the photodissociation result. This discrepancy between the photodissociation and kinetics values is not resolved. We favor the photodissociation results because the H_2CO reactant and HCO product spectra appear to be well characterized and resolved. The electron affinity of HCO from photoelectron spectroscopy[39] is $EA_0(HCO) = 0.313 \pm 0.005$ eV $= 30.2 \pm 0.5$ kJ/mol. Combining the dissociation energy[37] and the electron affinity[39] yields $\Delta_{acid}H_0(H_2CO) = 1644.7 \pm 0.5$ kJ/mol.

Water. The electron affinity of hydroxyl radical from laser photodetachment threshold measurements[40] is $EA_0(OH) = 14741.02 \pm 0.03$ cm^{-1} $= 176.3418 \pm 0.0004$ kJ/mol. Until recently, the accepted value for the bond dissociation energy of water[23,25] was based on spectroscopic extrapolation of the vibrational levels of OH to the dissociation limit, combined with established enthalpies of formation of H, O, and H_2O to give $D_0(HO{-}H) = 494.07 \pm 0.21$ kJ/mol. However, two recent independent experimental measurements[19,25,26] and a theoretical analysis[19,25] show convincingly that a lower value is correct. Using the measured dissociative photoionization threshold energy for OH^+ from H_2O and related ionization energies, Ruscic et al.[19,25] obtain $D_0(HO{-}H) = 117.59 \pm 0.07$ kcal/mol $= 492.00 \pm 0.29$ kJ/mol. Harich et al.[26] use rotationally resolved photofragment translation spectroscopy of H_2O to obtain $D_0(HO{-}H) = 41151 \pm 5$ cm^{-1} $= 492.28 \pm 0.06$ kJ/mol. The agreement between these two experiments (apparently unknown to each other at the times of publication) strongly supports the revision from the previously accepted value. Ruscic et al.[19,25] also employ high-level theoretical calculations to show that standard extrapolations of the OH vibrational energy levels do not give the true dissociation limit. Using the precise photodissociation result in eq 1 yields $\Delta_{acid}H_0(H_2O) = 1627.98 \pm 0.06$ kJ/mol. The photoion-pair threshold energy[1] is $\Delta_{acid}H_0(H_2O) = 16.87 \pm 0.03$ eV $= 1628 \pm 3$ kJ/mol, less precise but in good agreement. We adopt the value from eq 1.

Ethyne. The bond dissociation energy of acetylene was controversial at one time,[41−44] but several independent experimental measurements[12,45−48] around 1990 converged at values near the more recent and higher resolution photofragment translational spectroscopy result,[49] $D_0(HCC{-}H) = 46074 \pm 8$ cm^{-1} $= 551.2 \pm 0.1$ kJ/mol. The electron affinity of the ethynyl radical from negative ion photoelectron spectroscopy[50] is $EA_0(C_2H) = 2.969 \pm 0.006$ eV $= 286.5 \pm 0.6$ kJ/mol. An independent measurement[51] at lower resolution, $EA_0(C_2H) = 2.956 \pm 0.020$ eV, confirms the electron affinity. The dissociation energy[49] and electron affinity[50] can be combined to give the acidity, $\Delta_{acid}H_0(HCCH) = 1576.8 \pm 0.6$ kJ/mol, which we adopt and which agrees well with the photoion-pair threshold energy[47] of $\Delta_{acid}H_0(HCCH) = 16.335 \pm 0.02$ eV $= 1576.1 \pm 1.9$ kJ/mol.

Hydrogen Fluoride. The spectroscopic dissociation limit of HF has been reported[52] as $D_0(HF) = 47311 \pm 5$ cm^{-1} $= 565.97 \pm 0.06$ kJ/mol, and the electron affinity of fluorine atom from photodetachment experiments[53,54] is $EA_0(F) = 27432.440 \pm 0.025$ cm^{-1} $= 328.1649 \pm 0.00030$ kJ/mol, which combine to yield $\Delta_{acid}H_0(HF) = 1549.85 \pm 0.06$ kJ/mol. The gas-phase acidity of HF from the direct process $HF \rightarrow H^+ + F^-$ in TIPPS experiments[55] is $\Delta_{acid}H_0(HF) = 129557.7 \pm 1$ cm^{-1} $= 1549.854 \pm 0.012$ kJ/mol, in excellent agreement. In pulsed-field ionization photoelectron spectroscopy of HF,[56] a feature at 16.0622 ± 0.0005 eV is assigned to threshold ion-pair formation, yielding $\Delta_{acid}H_0(HF) = 1549.77 \pm 0.05$ kJ/mol, lower than the TIPPS value by 0.08 ± 0.05 kJ/mol. We favor the TIPPS result because the spectra are better resolved than the pulsed-field ionization spectra and because it is in better agreement with the negative ion thermochemistry cycle.

Hydrogen Sulfide. Using $D_0(HS{-}H) = 31440 \pm 40$ cm^{-1} $= 376.1 \pm 0.5$ kJ/mol from photofragment translational spectroscopy[57] and either $EA_0(SH) = 2.317 \pm 0.002$ eV $= 223.6 \pm 0.2$ kJ/mol from photodetachment threshold spectroscopy[58] or $EA_0(SH) = 18666.4 \pm 0.2$ cm^{-1} $= 223.300 \pm 0.024$ kJ/mol from photodetachment in an ion trap experiment (described as a "preliminary" value),[59] one obtains either $\Delta_{acid}H_0(H_2S) = 1464.6 \pm 0.5$ kJ/mol or 1464.9 ± 0.5 kJ/mol, respectively. Alternatively, the TIPPS spectrum of H_2S of Hepburn and co-workers[21] directly yields the gas-phase acidity, $\Delta_{acid}H_0(H_2S) = 122458 \pm 3$ cm^{-1} $= 1464.92 \pm 0.04$ kJ/mol, in best agreement with the electron affinity from ion trap photodetachment.[59] The TIPPS result is adopted here for the acidity because it is more direct and more precise than the values obtained from the negative ion cycle.

Hydrogen Cyanide. The electron affinity of the CN radical from negative ion photoelectron spectroscopy[60] is $EA_0(CN) = 3.862 \pm 0.004$ eV $= 372.6 \pm 0.4$ kJ/mol. The bond dissociation energy of hydrogen cyanide[61] from PTS of hydrogen atoms formed in the photodissociation of HCN is $D_0(H{-}CN) = 43710 \pm 70$ cm^{-1} $= 522.9 \pm 0.8$ kJ/mol. The H-atom translational spectra exhibit ro-vibrational structure assigned to electronically excited states of the CN fragment. Photoionization threshold measurements[1,62] on HCN give $D_0(H{-}CN) = 521.3 \pm 0.8$

TABLE 2: Gas-Phase Acidities at 298 K[a]

	present evaluation				NIST database[7]		
HA	$\Delta_{\mathrm{acid}}H_0(\mathrm{HA})$[b]/ kJ mol^{-1}	$\Delta_{\mathrm{acid}}H_{298}(\mathrm{HA})$/ kJ mol^{-1}	$\Delta_{\mathrm{acid}}S_{298}(\mathrm{HA})$/ J K^{-1} mol^{-1}	$\Delta_{\mathrm{acid}}G_{298}(\mathrm{HA})$/ kJ mol^{-1}	$\Delta_{\mathrm{acid}}G_{298}(\mathrm{HA})$/ kJ mol^{-1}	method[c]	ref[d]
CH_4	1737.0 ± 2.9	1744.1 ± 3.0	115.1 ± 1.6	1709.8 ± 3.0	1709.6 ± 3.3	D-EA	29
					1715. ± 15.	TCID	67
NH_3	1681.7 ± 0.5	1687.7 ± 0.5	105.2 ± 0.7	1656.4 ± 0.5	1660.6 ± 1.7	D-EA	30
					1657.3 ± 2.9	IMRE	68
H_2	1671.360 ± 0.012	1675.286 ± 0.012	87.23 ± 0.01	1649.279 ± 0.012	1649.	D-EA	35
H_2CO	1644.7 ± 0.5	1650.7 ± 0.8	111.3 ± 0.9	1617.5 ± 0.8	1613.4 ± 3.3	D-EA	39
					1648. ± 19.	Bracket	69
H_2O	1627.98 ± 0.06	1632.9 ± 0.1	92.54 ± 0.20	1605.3 ± 0.1	1607.1 ± 0.84	D-EA	70
HCCH	1576.8 ± 0.6	1582.8 ± 0.6	112.3 ± 1.2	1549.3 ± 0.7	1546.8 ± 3.3	D-EA	50
					1547.2 ± 2.5	IMRE	12
					1542. ± 8.4	IMRE	71
					1576.5 ± 2.5	IMRE	72
					1540. ± 21.	Bracket	73
HF	1549.854 ± 0.012	1553.649 ± 0.013	80.747 ± 0.020	1529.575 ± 0.013	1530.5 ± 1.3	D-EA	53
					1529. ± 8.4	IMRE	74
H_2S	1464.92 ± 0.04	1469.81 ± 0.07	89.780 ± 0.21	1443.04 ± 0.07	1443.1 ± 0.42	TIPPS	21
					1443. ± 8.4	IMRE	71
					1446. ± 8.4	IMRE	75
					1441. ± 13.	ENDO	76
HCN	1462.3 ± 0.9	1467.9 ± 0.9	103.7 ± 0.5	1437.0 ± 0.9	1427. ± 8.8	D-EA	60
					1438. ± 8.4	IMRE	71
$H^{35}Cl$	1391.122 ± 0.007	1394.876 ± 0.010	75.40 ± 0.02	1372.395 ± 0.010	1372.8 ± 0.42	TIPPS	20
					1372.8 ± 0.84	D-EA	77
					1374. ± 8.4	IMRE	78
HBr	1349.92 ± 0.20	1353.67 ± 0.20	73.74 ± 0.01	1331.68 ± 0.20	1331.8 ± 0.84	D-EA	53
					1331. ± 8.4	IMRE	79
HI	1311.42 ± 0.12	1315.16 ± 0.12	71.62 ± 0.01	1293.81 ± 0.12	1293.7 ± 0.84	D-EA	64

[a] Thermal enthalpy and entropy corrections are presented in the Supporting Information. [b] From Table 1. [c] D-EA, calculated via eq 1; TCID, threshold collision-induced dissociation; IMRE, ion−molecule reaction equilibrium measurement; Bracket, ion−molecule kinetic bracketing method; TIPPS, threshold ion-pair production spectroscopy; ENDO, ion−molecule reaction threshold energy measurement. [d] References cited in the NIST negative ion thermochemistry database.[7]

kJ/mol using eq 4, with touching error bars with the PTS result. We favor the PTS experiment[61] over the photoionization measurements[62] because the thresholds in the latter experiment are not especially sharp and because the photoion-pair threshold combined with the H^+ appearance energy in the same experiment gave an electron affinity that is too low by 4 ± 2 kJ/mol, compared with the value from photoelectron spectroscopy. Adopting the bond energy from PTS[61] yields $\Delta_{\mathrm{acid}}H_0(\mathrm{HCN}) = 1462.3 \pm 0.9$ kJ/mol via eq 1.

Hydrogen Chloride. Threshold ion-pair production spectroscopy[20] of HCl yields $\Delta_{\mathrm{acid}}H_0(\mathrm{H^{35}Cl}) = 116288.7 \pm 0.6$ cm^{-1} $= 1391.122 \pm 0.007$ kJ/mol. The dissociation energy derived from calorimetric measurements of the enthalpy of the reaction between chlorine and hydrogen is $D_0(\mathrm{H^{35}Cl}) = 427.768 \pm 0.10$ kJ/mol (corrected for isotopic abundances).[23,34] The electron affinity from photodetachment threshold experiments[63] is $\mathrm{EA}_0(^{35}\mathrm{Cl}) = 29138.59 \pm 0.22$ cm^{-1} $= 348.5749 \pm 0.0026$ kJ/mol. The resulting acidity from the negative ion cycle is $\Delta_{\mathrm{acid}}H_0(\mathrm{H^{35}Cl}) = 1391.24 \pm 0.10$ kJ/mol. This value is barely outside the error bars of the more direct and precise TIPPS value, which we adopt.

Hydrogen Bromide. The dissociation energy of hydrogen bromide is $D_0(\mathrm{HBr}) = 362.41 \pm 0.20$ kJ/mol, from calorimetric measurements of the enthalpy of solution of HBr in water.[23,34] The electron affinity of atomic bromine is $\mathrm{EA}_0(\mathrm{Br}) = 27129.170 \pm 0.015$ cm^{-1} $= 324.53694 \pm 0.00018$ kJ/mol from laser photodetachment threshold measurements.[53] The resulting acidity is $\Delta_{\mathrm{acid}}H_0(\mathrm{HBr}) = 1349.92 \pm 0.20$ kJ/mol.

Hydrogen Iodide. The recommended bond dissociation energy of hydrogen iodide, $D_0(\mathrm{HI}) = 294.52 \pm 0.12$ kJ/mol, is based upon the enthalpy of solution of HI in water.[23,34] The photodetachment threshold wavelength for the iodine atom was determined[64] as 405.3047 ± 0.0013 nm, which gives the electron affinity, $\mathrm{EA}_0(\mathrm{I}) = 24672.795 \pm 0.080$ cm^{-1} $= 295.1522 \pm 0.0010$ kJ/mol. Using the negative ion cycle gives the acidity, $\Delta_{\mathrm{acid}}H_0(\mathrm{HI}) = 1311.42 \pm 0.12$ kJ/mol.

Comparison with the Gas-Phase Acidity Scale at 298 K from Equilibrium Measurements

The 0 K deprotonation energies in Table 1 are converted to enthalpies and Gibbs energies at 298.15 K, $\Delta_{\mathrm{acid}}H_{298}$ and $\Delta_{\mathrm{acid}}G_{298}$, in Table 2. Maintaining high precision requires careful consideration of the thermal corrections.[65,66] We use enthalpy and entropy corrections primarily from the evaluated thermodynamic functions of Gurvich et al.[23,24] Four of the anions, CH_3^-, NH_2^-, HCO^-, and C_2H^-, are not included in the compilation by Gurvich et al.[23,24] For these species, we calculate the thermal corrections by statistical mechanics using experimental or theoretical molecular constants, as presented in the Supporting Information.

Table 2 compares the present values for $\Delta_{\mathrm{acid}}G_{298}$ with those from the NIST negative ion thermochemistry database.[7] The correspondence is excellent for most species (some are based on the same experimental data). Significant revisions are found for the acidities of ammonia, formaldehyde, water, and hydrogen cyanide, compared with the first-listed values in the database. For ammonia, hydrogen fluoride, and hydrogen cyanide, the matches are better (ignoring uncertainties) with acidities in the database[7] from ion−molecule reaction equilibrium experiments than with those derived using eq 1. For the latter, the database[7] cites the literature for the electron affinities but not the source of the dissociation energies, so detailed comparisons are not possible.

TABLE 3: Thermochemistry of Alkanols, Ethene, and Benzene[a]

HA	$\Delta_{acid}H_0$ (HA)/ kJ mol^{-1}	EA$_0$(A)/ eV	D_0 (HA)/ kJ mol^{-1}	D_{298} (HA)/ kJ mol^{-1}	$\Delta_f H_{298}$(HA)/ kJ mol^{-1}	$\Delta_f H_{298}$(A)/ kJ mol^{-1}	$\Delta_{acid}H_{298}$(HA)/ kJ mol^{-1}	$\Delta_{acid}S_{298}$(HA)/ J K^{-1} mol^{-1}	$\Delta_{acid}G_{298}$(HA)/ kJ mol^{-1}
CH_3OH	1593.0 ± 2.3 [1594 ± 3][b]	1.570 ± 0.006 [c]	432.4 ± 2.4	437.7 ± 2.8	−201.5 ± 0.2[g]	18.2 ± 2.8	1597.9 ± 2.3	89.9 ± 1.2	1571.1 ± 2.4
CH_3CH_2OH	1579.8 ± 3.1 [1581 ± 5][b]	1.712 ± 0.004[d]	432.9 ± 3.1	438.1 ± 3.3	−235.2 ± 0.3[g]	−15.1 ± 3.3	1584.6 ± 3.2	90.0 ± 2.5	1557.7 ± 3.3
$(CH_3)_2CHOH$	1570.8 ± 2.6 [1571 ± 4][b]	1.847 ± 0.004[d]	437.0 ± 2.6	442.3 ± 2.8	−272.6 ± 0.5[g]	−48.3 ± 2.8	1575.8 ± 3.0	91.7 ± 3.0	1548.4 ± 3.1
$(CH_3)_3COH$	1567.3 ± 1.9 [1568 ± 3][b]	1.909 ± 0.004[d]	439.4 ± 2.1	444.9 ± 2.8	−312.5 ± 0.8[g]	−85.6 ± 2.9	1572.5 ± 2.8	93.1 ± 3.5	1544.7 ± 3.0
C_2H_4	1704.4 ± 1.2	0.667 ± 0.024[e]	456.7 ± 2.7	463.0 ± 2.7	52.5 ± 0.3[g]	297.5 ± 2.7	1710.4 ± 1.2	117.4 ± 1.5	1675.4 ± 1.1 [1677.8 ± 2.1][h]
C_6H_6	1672.1 ± 1.8	1.096 ± 0.006[f]	465.8 ± 1.9	472.2 ± 2.2	82.6 "0.7[g]	336.8 ± 2.3	1678.5 ± 0.8	124.4 ± 2.0	1641.4 ± 0.6 [1643.9 ± 1.7][i]

[a] Thermal enthalpy and entropy corrections are presented in the Supporting Information. [b] As originally reported by DeTuri and Ervin.[8] [c] Average of two recent negative ion photoelectron spectroscopy (PES) experiments, $EA_0(CH_3O) = 1.568 \pm 0.005$ eV from Osborn et al.[83] and 1.572 ± 0.004 eV from Ramond et al.[82] [d] PES, Ramond et al.[82] [e] PES, Ervin et al.[12] [f] PES, Gunion et al.[92] [g] From compilation by Pedley.[93] [h] As originally reported by Ervin et al.[12] [i] As originally reported by Davico et al.[13]

In several instances, proton-transfer equilibrium measurements have been made directly relating the acidities of two of the anchor acids in Table 2. Bohme and co-workers[80] measured the equilibrium for the reaction $NH_2^- + H_2 \rightleftarrows NH_3 + H^-$ by the flowing afterglow technique and found $\Delta_r G_{297} = -1.9 \pm 0.2$ kJ/mol $= -7.9 \pm 0.8$ kJ/mol, compared with $\Delta\Delta_{acid}G = -7.1 \pm 0.5$ kJ/mol from Table 2, in agreement within the uncertainties. For the reaction $SH^- + HCN \rightleftarrows H_2S + CN^-$, the measured acidity differences by Bohme and co-workers,[81] $\Delta_r G_{296} = -1.6 \pm 0.1$ kcal/mol $= -6.7 \pm 0.4$ kJ/mol, agrees with -6.0 ± 0.9 kJ/mol from Table 2. For the same reaction, Bartmess et al.[71] found $\Delta_r G_{296} = -1.1 \pm 0.2$ kcal/mol $= -4.6 \pm 0.8$ kJ/mol, in ion cyclotron resonance equilibrium measurements. The Bohme group[72] found $\Delta_r G_{296} = -7.3 \pm 0.2$ kcal/mol $= -30.5 \pm 0.8$ kJ/mol for the reaction $OH^- + C_2H_2 \rightleftarrows H_2O + HCC^-$, in obvious disagreement with the result $\Delta\Delta_{acid}G = -56.0 \pm 0.7$ kJ/mol from Table 2. This experiment[72] relied on measurement of an extremely small rate constant for the reverse reaction, $k \approx 10^{-14}$ cm^3 s^{-1}. In hindsight, the observed reaction of HCC^- was probably due to an impurity or side reaction. Ervin et al.[12] reported the acidity difference between HF and acetylene from selected-ion flow tube measurements of the forward and reverse rate coefficients for the reaction $F^- + HCCH \rightleftarrows HF + HCC^-$. The reported value, $\Delta_r G_{300} = +4.27 \pm 0.20$ kcal/mol $= 17.8 \pm 0.8$ kJ/mol differs from $\Delta\Delta_{acid}G = 19.7 \pm 0.7$ kJ/mol from Table 2 by 1.8 kJ/mol, which is slightly greater than the combined uncertainties. However, the acetylene acidity reported in the same work,[12] $\Delta_{acid}G_{298}(HCCH) = 1547.2 \pm 2.5$ kJ/mol, incorporating additional equilibrium measurements involving iso-propyl and *tert*-butyl alcohol, agrees with the value of $\Delta_{acid}G_{298}(HCCH) = 1549.3 \pm 0.7$ kJ/mol in Table 2 within the stated uncertainty. A high-resolution TIPPS measurement of the acidity might help improve the internal consistency of the negative ion cycle for HCCH.

Application of the Revised Acidity Scale to Alkanol, Ethene, and Benzene Acidities

In this section, we revisit several previous gas-phase acidity measurements, including our own work, that are affected by revisions to acidities of anchor species. Thermal corrections between 0 and 298 K are calculated by statistical mechanics from experimental and theoretical molecular parameters presented in the Supporting Information. The results are summarized in Table 3.

Alkanols. We previously reported energy-resolved competitive threshold collision-induced dissociation (TCID) experiments on proton-bound $RO^-(HX)$ complexes (eq 3), using guided ion beam tandem mass spectrometry.[8] We studied the small alkanols ROH = methanol, ethanol, 2-propanol (iso-propyl alcohol), and 2-methyl-2-propanol (*tert*-butyl alcohol). HX represents a different alcohol or the reference acid H_2O or HF. The energy-dependent branching ratios between the two product channels in eq 3 are modeled using RRKM theory.[8,10,11] The data analysis accounts for kinetic and competitive shifts, internal energy effects, and the experimental kinetic energy distribution,[8,10,11] yielding the gas-phase acidity difference between ROH and HX at 0 K. The experimental uncertainty[8] of individual relative acidities is ±3 to ±5 kJ/mol (±2 combined standard uncertainties[28]). The accuracy of derived absolute acidities can be improved by a least-squares analysis of a ladder of multiple interlocking relative measurements among the alkanols and the reference acids. Using a “local thermochemical network”[18] of this type automatically gives higher weight to more precise measurements or standards and provides uncertainties that incorporate both the experimental uncertainties of individual measurements and the consistency or inconsistency of thermochemical cycles.

In our previous report,[8] measurements of 18 individual TCID experiments were combined to determine the acidities of the four alkanols anchored to H_2O and HF as depicted by the acidity ladder in Figure 2. A least-squares analysis of this thermochemical network originally yielded the 0 K gas-phase acidities given in square brackets in the second column of Table 3. However, when HF was treated as the single standard and H_2O was treated as an additional unknown, we noted[8] that the derived acidity for H_2O was 2 ± 2 kJ/mol lower than the accepted value. At the time, we considered that error simply a reflection of the uncertainty of the method. However, the recent revisions[19,26] of the bond energy of water discussed above lower the acidity by 1.8 kJ/mol, precisely accounting for the apparent error. Revised acidities from a new least-squares analysis incorporating the revised acidity of H_2O are listed in Table 3 and Figure 2. The uncertainties of the revised acidities are smaller than those previously reported because of the improved internal consistency of the network.

These revised gas-phase acidities of the alkanols can be used in the negative ion thermochemical cycle (eq 1) to obtain OH bond dissociation enthalpies. The electron affinities of the alkoxy radicals, listed in Table 2 along with the derived dissociation energies, have been measured by negative ion photoelectron spectroscopy.[82,83] The OH bond dissociation enthalpies at 298 K for the series methyl, ethyl, iso-propyl, and *tert*-butyl alcohol, $D_{298}(RO{-}H) = 437.7 \pm 2.8$, 438.1 ± 3.3, 442.3 ± 2.8, and

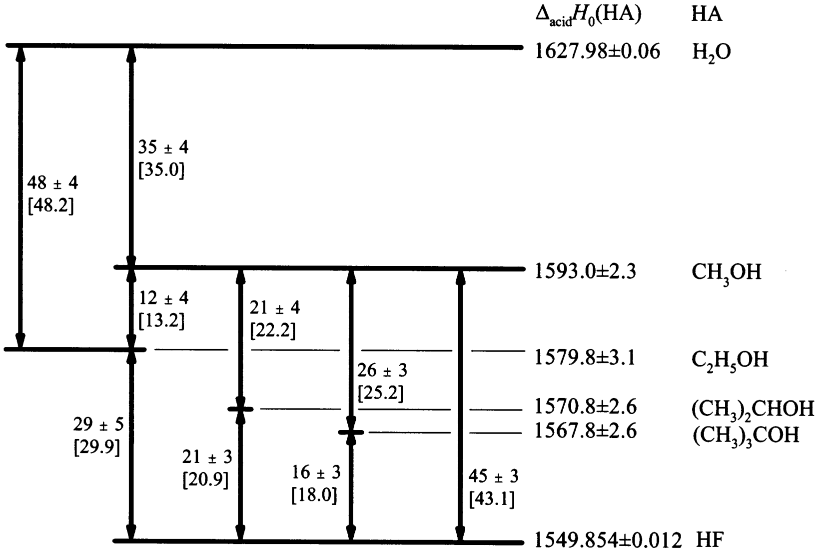

Figure 2. Gas-phase acidity network for alkanols from competitive threshold collision-induced dissociation experiments.[8] The experimental relative acidities for individual acid pairs (mean values for multiple measurements) are shown next to the arrows. The reanchored absolute acidities obtained by least-squares analysis of the thermochemical network are listed on the right-hand side and the corresponding relative acidities are given in square brackets. All values are in kJ/mol.

444.9 ± 2.8 kJ/mol, respectively, can be compared with the values from kinetics experiments recommended by McMillen and Golden:[84] 436.8, 436.0, 438.1, and 439.7 kJ/mol, respectively, with estimated uncertainties of 4.2 kJ/mol. The values for the primary alcohols agree well, but we find a stronger increase in the dissociation energy for the secondary and tertiary alcohols. The smaller uncertainties from the present analysis make this trend more clear than before.[8]

For methanol, our OH bond dissociation energy of $D_0(CH_3O-H) = 432.4 \pm 2.4$ kJ/mol can also be compared with $D_0(CH_3O-H) = 104.0 \pm 0.5$ kcal/mol $= 435.1 \pm 2.1$ kJ/mol derived from negative ion photodetachment/photofragment translational spectroscopy experiments[85] on CH_3O^-. These values are in fair agreement, with overlapping error bars. It would be useful to have a higher-resolution spectroscopic measurement of this important bond energy. For ethanol, our bond dissociation energy of $D_0(C_2H_5O-H) = 432.9 \pm 3.1$ kJ/mol agrees well with an upper limit from translational energy release in photodissociation experiments,[86] $D_0(C_2H_5O-H) \leq 433.9 \pm 2.1$ kJ/mol.

Ethene. A measurement of the gas-phase acidity of ethylene was obtained from a selected-ion flow tube reactor study[12] of the forward and reverse rates of the proton-transfer reaction $C_2H_3^- + NH_3 \rightleftarrows C_2H_4 + NH_2^-$. That work finds $\Delta_rG_{298} = +4.54 \pm 0.24$ kcal/mol $= 19.0 \pm 1.0$ kJ/mol. Combined with the ammonia acidity from Table 2, this yields $\Delta_{acid}G_{298}(C_2H_4) = 1675.4 \pm 1.1$ kJ/mol. This acidity is outside the error bars of the originally reported value (Table 3) because of the revision of the gas-phase acidity of ammonia. The electron affinity of vinyl radical from negative ion photoelectron spectroscopy[12] is $EA_0(C_2H_3) = 0.667 \pm 0.024$ eV $= 64.4 \pm 2.3$ kJ/mol. The negative ion thermochemical cycle gives the bond dissociation energy of ethene (Table 3), $D_0(C_2H_3-H) = 456.7 \pm 2.7$ kJ/mol or $D_{298}(C_2H_3-H) = 463.0 \pm 2.7$ kJ/mol.

This ethene bond dissociation energy can be compared with three recent radical kinetics measurements. In separate kinetics measurements of the reaction $Cl + C_2H_4 \rightarrow HCl + C_2H_3$ combined with the reverse activation energy from Russel et al.,[87] Kaiser and Wallington[88] obtain $\Delta_rH_{298} = 7.06 \pm 0.4$ kcal/mol $= 29.5 \pm 1.7$ kJ/mol, and Pilgrim and Taatjes[89] obtain $\Delta_rH_{298} = 7.33 \pm 0.3$ kcal/mol $= 30.7 \pm 1.3$ kJ/mol, both using third-law analyses. Using $D_{298}(HCl) = 431.61 \pm 0.10$ kJ/mol from Gurvich et al.,[23,24] these yield $D_{298}(C_2H_3-H) = 461.1 \pm 1.7$ kJ/mol and 462.3 ± 1.3 kJ/mol, from the two experiments, respectively. In independent experiments, Kynazev and Slagle[90] examined the forward and reverse kinetics of the reaction $C_2H_3 \rightleftarrows C_2H_2 + H$ and found $\Delta_rH_{298} = 147.3 \pm 14$ kJ/mol (or ±7 if their theoretical model is assumed to be correct). Using auxiliary thermochemical data for C_2H_2, C_2H_4, and H from Gurvich et al.,[23,24] this measurement yields $D_{298}(C_2H_3-H) = 464 \pm 14$ kJ/mol. These three dissociation enthalpies are in good agreement with each other and with the negative ion cycle value from above. The mutual agreement is improved by the revision of the ammonia acidity and the use of consistent auxiliary thermochemical values. Together they support a higher value for the CH bond dissociation enthalpy of ethylene compared with values of 442−446 kJ/mol from earlier kinetics measurements.[87,91] Other previous experiments are reviewed elsewhere.[1,12,87]

Benzene. The equilibrium $C_6H_5^- + NH_3 \rightleftarrows C_6H_6 + NH_2^-$ was examined by Davico et al.,[13] who measured the forward and reverse reaction rate coefficients by the flowing afterglow/selected ion flow tube technique, giving $\Delta_rG_{300} = -3.58 \pm 0.06$ kcal/mol $= -14.98 \pm 0.25$ kJ/mol. Combined with the gas-phase acidity of ammonia in Table 2, this yields $\Delta_{acid}G_{298}(C_6H_6) = 1641.4 \pm 0.6$ kJ/mol. This revised acidity is lower than the originally reported value[13] (Table 3) by 2.8 kJ/mol, more than the original error bars, because of the revision of the ammonia acidity. The electron affinity of the phenyl radical from photoelectron spectroscopy[92] is 1.096 ± 0.006 eV. Using eq 1 and thermal corrections presented in the Supporting Information, the revised bond dissociation enthalpy is $D_{298}(C_6H_5-H) = 472.2 \pm 2.2$ kJ/mol. That is still on the high side of the formerly recommended value of $D_{298}(C_6H_5-H) = 464 \pm 8$ kJ/mol from kinetics experiments.[84] Davico et al.[13] have discussed other previous measurements of the benzene CH bond dissociation energy.

The bond dissociation energies may be combined with literature enthalpies of formation of the parent molecules to obtain enthalpies of formation of the radicals. These are also presented in Table 3. For the parent enthalpies of formation,

TABLE 4: Comparison of Theoretical and Experimental Gas-Phase Acidities, $\Delta_{acid}H_0$(RH)/kJ mol^{-1}

	G3//B3LYP		CBS-QB3		B3LYP[a]						CCSD(T)//B3LYP[a]						
acid	—	δ[b]	—	δ	DZ[c]	δ	TZ//DZ[d]	δ	TZ[e]	δ	DZ[f]	δ	TZ[g]	δ	QZ//TZ[h]	δ	expt[i]
CH_4	1749.9	12.9	1747.5	10.5	1726.2	−10.8	1733.0	−4.0	1732.9	−4.1	1729.2	−7.8	1737.2	0.2	1737.6	0.6	1737.0 ± 2.9
C_2H_4	1706.6	2.2	1704.2	−0.2	1689.9	−14.5	1698.3	−6.1	1698.3	−6.1	1689.9	−14.5	1700.1	−4.3	1701.8	−2.6	1704.4 ± 1.2
NH_3	1689.3	7.6	1688.1	6.4	1673.0	−8.7	1678.5	−3.2	1678.5	−3.2	1675.4	−6.3	1682.2	0.5	1682.8	1.1	1681.7 ± 0.5
C_6H_6	1670.8	−1.3	1669.4	−2.7	1664.0	−8.1	1674.9	2.8	1673.2	1.1	1656.9	−15.2	1668.4	−3.7			1672.1 ± 1.8
H_2	1679.7[j]	8.3	1676.0[j]	4.7	1653.7	−17.7	1665.2	−6.2	1665.7	−5.7	1656.5	−14.8	1670.2	−1.1	1671.9	0.6	1671.360 ± 0.012
H_2CO	1650.5	5.8	1654.8	10.1	1625.0	−19.7	1633.6	−11.1	1633.6	−11.1	1635.4	−9.3	1644.6	−0.1	1645.0	0.3	1644.7 ± 0.5
H_2O	1633.2	5.3	1635.3	7.3	1614.7	−13.3	1620.5	−7.5	1620.5	−7.5	1620.7	−7.3	1628.2	0.3	1629.1	1.1	1627.98 ± 0.06
CH_3OH	1600.5	7.5	1595.8	2.8	1574.2	−18.8	1580.8	−12.2	1580.8	−12.2	1585.7	−7.3	1594.1	1.1	1594.2	1.2	1593.0 ± 2.3
CH_3CH_2OH	1583.8	4.0	1580.0	0.2	1562.8	−17.0	1568.8	−11.0	1568.8	−11.0	1572.2	−7.6	1580.5	0.7			1579.8 ± 3.1
HCCH	1579.7	2.9	1576.9	0.1	1561.1	−15.7	1574.3	−2.5	1574.4	−2.4	1557.1	−19.7	1573.5	−3.3	1574.9	−1.9	1576.8 ± 0.6
$(CH_3)_2CHOH$	1572.8	2.6	1570.0	−0.8	1556.6	−14.2	1562.0	−8.8	1562.0	−8.8	1563.5	−7.3	1571.6[k]	0.8			1570.8 ± 2.6
$(CH_3)_3COH$	1566.4	−0.9	1564.1	−3.2	1554.9	−12.4	1559.6	−7.7	1559.3	−8.0	1559.1	−8.2	1566.5	−0.8			1567.3 ± 1.9
HF	1552.5	2.7	1555.8	6.0	1525.8	−24.1	1535.8	−14.0	1535.8	−14.0	1537.9	−12.0	1551.1	1.2	1551.7	1.8	1549.854 ± 0.012
H_2S	1464.7	−0.2	1462.8	−2.1	1450.9	−14.0	1460.2	−4.8	1460.3	−4.6	1459.9	−5.1	1466.0	1.1	1464.9	-0.0_2	1464.92 ± 0.04
HCN	1464.8	2.5	1461.0	−1.3	1449.4	−12.9	1459.3	−3.0	1459.4	−2.9	1451.0	−11.3	1461.5	−0.8	1461.5	−0.8	1462.3 ± 0.9
HCl	1392.2	1.1	1386.1	−5.0	1372.8	−18.3	1383.7	−7.4	1383.9	−7.2	1384.5	−6.6	1395.5	4.4	1392.1	1.0	1391.122 ± 0.007
HBr	n/a[l]		n/a[l]		1336.8	−13.1	1345.6	−4.3	1345.6	−4.3	1351.3	1.4	1361.1	11.2	1357.0	7.1	1349.92 ± 0.20
mean error[l]		+3.9		+2.1		−15.0		−6.7		−6.6		−10.0		−0.2		+0.2[m]	
std. dev.[l]		3.9		4.9		4.2		4.3		4.0		4.1		2.2		1.3[m]	0.40[n]
mean abs. dev.[l]		4.2		4.0		15.0		7.0		6.7		10.0		1.5		1.1[m]	1.06[o]
maximum error		+12.9		+10.5		−24.1		−14.0		−14.0		−19.7		+11.2		+7.1	

[a] Zero-point energy corrections from unscaled frequencies at the B3LYP/aug-cc-pVDZ level. [b] δ = theory − experiment. [c] B3LYP/aug-cc-pVDZ. [d] B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVDZ. [e] B3LYP/aug-cc-pVTZ. [f] CCSD(T)/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ. [g] CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ. [h] CCSD(T)/aug-cc-pVQZ//B3LYP/aug-cc-pVTZ. [i] Tables 1 and 3. [j] Using accurate theoretical energy for H^- (see text). Pure G3//B3LYP and CBS-QB3 acidities for H_2 are $\Delta_{acid}H_0 = 1701.8$ and 1697.3 kJ/mol, respectively. [k] Because of computational limitations, the energy of iso-propyl alcohol was calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level for the more symmetric trans conformation, and then corrected by 1.1 kJ/mol for the more stable gauche conformation based on B3LYP/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ energy differences. [l] Bromine is not available in the standard Gaussian 98 basis sets[94] for G3//B3LYP and CBS-QB3. HBr is excluded from the error statistics for all methods. [m] For subset of acids calculated at the QZ level. [n] Root-mean-square uncertainty. [o] Mean absolute uncertainty.

we have used the evaluated values from the compilation of organic thermochemistry by Pedley.[93]

Investigation of ab Initio Gas-Phase Acidities

In Table 4, we present gas-phase acidities at 0 K calculated at several levels of theory using Gaussian 98.[94] First, we use the model thermochemistry methods, Gaussian-3//B3LYP[14,95] and the complete basis set extrapolation, CBS-QB3.[15] Because of the known deficiencies[96,97] of the Gaussian-*n* and CBS models for H^- owing to lack of diffuse functions on hydrogen, the accurate theoretical value[5] of $E(H^-) = 0.5277165$ Hartree was substituted. Figure 3 shows histograms of the deviations between experiment and theory (δ = theory − experiment). The performance of these model thermochemistry methods is within the target accuracy in most cases. The G3 and CBS absolute acidities are on average 3.8 and 1.9 kJ/mol higher than experiment, and the maximum errors are 12.8 and 10.5 kJ/mol, respectively, for CH_4. The variance of the individual deviations around the mean error (represented statistically by the standard deviation of 4−5 kJ/mol or a 95% confidence interval of about ±8 to ±10 kJ/mol) is on the same order of magnitude as the uncertainty of the equilibrium gas-phase acidity scale. Pokon et al.[98] recently compared acidities from the G3, CBS-QB3, and CBS-APNO models for 17 acids with 2−10 first- and second-row atoms and experimental uncertainties within 4 kJ/mol according to the NIST database.[7] Their set of acids includes most of those in Table 1 and also several amines, isocyanic acid, nitric acid, furan, allene, ethene, and benzene. Our CBS-QB3 acidities agree with theirs for the same species, and the overall performance found for the two different sets of acids is similar. Pokon et al.[98] found mean absolute deviations of 3.8−5.3 kJ/mol between experiment and the three model thermochemistry methods for $\Delta_{acid}H_{298}$, compared with the mean absolute deviations of 4.2 and 4.0 kJ/mol for G3//B3LYP and CBS-QB3, respectively, for $\Delta_{acid}H_0$ found here. Maximum deviations here and in the work of Pokon et al. are in the 10−15 kJ/mol range, however, which is large compared with the experimental uncertainties.

Our next goal is to determine whether higher-level calculations using widely available methods can yield acidities that are sufficiently accurate to identify problem cases, as gauged against our set of acidities in Tables 1 and 3. Geometries and frequencies are calculated with density functional theory (DFT) using the Becke3/Lee−Yang−Parr (B3LYP) hybrid functional[99] with the "tight" SCF convergence and geometry optimization criteria and the "ultrafine" integration grid in Gaussian 98.[94] Correlation-consistent basis sets[100−102] are used, aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ (abbreviated DZ, TZ, and QZ here). Spin-restricted, frozen-core coupled-cluster calculations, CCSD(T),[103] are employed for single-point energies at the DFT geometries. The CCSD(T)/TZ single-point calculations are the largest feasible for the acidity of C_4H_9OH with our computational facilities, requiring six weeks on a dedicated XP1000 667 MHz Compaq Alpha workstation with 1.5 GB of random access memory and 32 GB of hard disk space. Because of memory limitations, we were unable to complete the CCSD(T)/TZ calculation for gauche $(CH_3)_2CHOH$ (C_1), which is smaller overall than *tert*-butyl alcohol but is asymmetric. Instead, we calculated the *trans* $(CH_3)_2CHOH$ (C_s) conformation and corrected using the conformational energy difference from lower-level calculations (see Table 4). Vibrational zero-point energies (ZPEs) are calculated from harmonic frequencies at the B3LYP/DZ level without scaling. Using the scaling factor of 0.98 recommended[104] for ZPEs for B3LYP/6-31G(d) calculations would raise the mean acidities by 0.7 kJ/mol. The empirical scaling factor has not been determined specifically for the

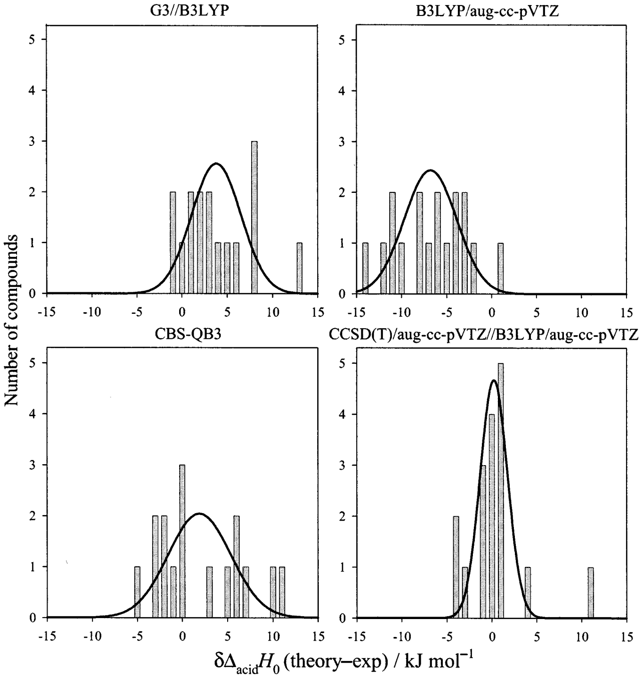

Figure 3. Comparison between experimental and theoretical deprotonation energies at 0 K for the acids in Table 4. Histograms of the deviations (δ = theory − experiment) are shown for the G3//B3LYP, CBS-QB3, B3LYP/aug-cc-pVTZ, and CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ levels of theory. The superimposed Gaussian curves represent the statistical mean and standard deviation of the deviations between theory and experiment (excluding HBr, which is not available for the G3//B3LYP and CBS-QBS methods). Outliers may be identified by reference to Table 4.

B3LYP/DZ level but should be close to 1.00 ± 0.01 assuming the same trend with basis set size is followed as observed for Hartree−Fock calculations.[104]

Comparing the DFT results for DZ, TZ//DZ, and TZ optimizations in Table 4 shows that the larger basis set is important for energies but that the geometry change from the double- to triple-ζ basis set does not greatly affect the results. The mean absolute error is 6.9 kJ/mol at the B3LYP/TZ level. For a more diverse set of 49 gas-phase acids, Burk et al.[105] found a mean absolute error of 9.6 kJ/mol in $\Delta_{\text{acid}}G$ at the B3LYP/6-311+G(3df,3pd) level. Merrill and Kass[106] compared various DFT functionals and basis sets for calculating gas-phase acidities of 35 species. They found the best results (mean errors of 5 to 8 kJ/mol) using a hybrid functional, B3−PW91, but did not test the B3LYP hybrid functional used here, and found similar performance for both Pople-type basis sets and Dunning's correlation-consistent basis sets (the latter are used here).

Comparing CCSD(T) to B3LYP for either the DZ or the TZ basis set demonstrates that the higher-level treatment of electron correlation has a significant effect on the absolute acidities. As also shown in Figure 3, the mean (signed) error at the B3LYP/TZ level is −6.8 kJ/mol, but at the CCSD(T)/TZ//B3LYP/TZ level, it is reduced to −0.2 kJ/mol, well within the experimental uncertainties and the uncertainty of the vibrational ZPE correction. The standard deviation is reduced from 4.1 to 2.1 kJ/mol for the same two calculations. Calculations on selected small systems at the CCSD(T)/QZ//B3LYP/TZ level (Table 4) show modest additional changes in the acidities, but with notable improvements for C_2H_4, HCCH, and HCl. The excellent agreement between experiment and theory for the CCSD(T)/TZ and CCSD(T)/QZ single-point calculations for molecules with elements through chlorine corroborate the reevaluated experimental acidities. For example, the deviations for the acidities of the four alkanols discussed above show a strong systematic size dependence at the G3, CBS, and B3LYP levels of theory in Table 4, but that effect is nearly eliminated at the CCSD(T) level.

Most of the individual deviations for the CCSD(T)/TZ//B3LYP/TZ values in Table 4 and Figure 3 are clustered between $\delta = -1.2$ to $+ 1.2$ kJ/mol, i.e., showing excellent performance. The exceptions are HBr ($\delta = 11.2$ kJ/mol), HCl (4.4), HCCH (−3.3), C_6H_6 (−3.7), and C_2H_4 (−4.5). One can never absolutely rule out experimental errors, but these species appear to have well-established acidities. Hydrogen bromide is clearly an outlier. The heavier halogens and other heavy elements may require treatment of relativistic effects and core electron correlation or larger basis sets with more diffuse and polarization functions. Hydrogen chloride may have a small residual error for the same reasons, but its error is largely eliminated with the CCSD(T)/QZ single-point calculation. Ethylene, acetylene, and acetylene all have carbon−carbon π bonds, suggesting that a higher-level treatment of correlation or larger basis sets might be required for benchmark quality agreement with experiment for carbon π systems. The acidities for C_2H_4 and C_2H_2 are improved by the QZ calculations, though not quite to within the experimental uncertainties. The performance of the CCSD(T)/TZ//B3LYP/TZ calculations is sufficiently good, for closed-shell compounds with primarily single bonds composed of elements up to chlorine, that a deviation between theoretical and experimental acidities of greater than 3 standard deviations (6 kJ/mol) implies that one should suspect a problem with the experimental value. With current computer technology, CCSD(T)/TZ calculations are feasible for species with up to 5−6 heavy atoms.

Summary

We have evaluated a set of 12 molecules with gas-phase acidities that are accurately known independently of proton transfer kinetics or equilibrium experiments. These anchor acids provide high-quality reference acidities for relative gas-phase acidity measurements. The evaluated acidities for ammonia, water, and formaldehyde are significantly different from previously recommended values. The results are summarized in Tables 1−2. We have employed these new acidities to reanchor previous relative gas-phase acidity measurements of simple alkanols, ethene, and benzene. The revised bond dissociation enthalpies, listed in Table 3, are significantly different from the originally reported values for the cases of ethene and benzene because of the revision of the ammonia acidity. The results for the alkanols shows that acidities obtained by the competitive threshold collision-induced dissociation method rivals the accuracy of other techniques when the relative acidities are firmly anchored to absolute acidities in a local thermochemical network. Improved bond dissociation enthalpies for the alkanols, ethylene, and benzene are also presented in Table 3.

We find that theoretical calculations of gas-phase acidities at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level provide excellent matches with experiment (mean error of −0.2 kJ/mol) for 16 closed shell molecules composed of elements through chlorine with mostly single bonds. The theoretical results corroborate the recommended revisions to experimental acidities. Acids with many multiple bonds or heavier elements may require a larger basis set or a higher level of electron correlation for acidity predictions of benchmark quality. Lower-level methods give reasonable results for acidities, as found in previous comparisons of experimental and theoretical gas-phase acidities,[98,106] but of less than benchmark quality.

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Supporting Information Available: Tables of the thermal corrections $H_{298} - H_0$ and S_{298} and the molecular parameters used to calculate them. Discussion of the statistical mechanics treatment of internal hindered rotors. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(2) Ervin, K. M. *Chem. Rev.* **2001**, *101*, 391.

(3) Ervin, K. M.; Lineberger, W. C. In *Advances in Gas-Phase Ion Chemistry*; Adams, N. G., Babcock, L. M., Eds.; JAI: Greenwich, CT, 1992; Vol. 1, p 121.

(4) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Nandi, S.; Ellison, G. B.; Schaefer, H. F., III. *Chem. Rev.* **2002**, *102*, 231.

(5) Andersen, T.; Haugen, H. K.; Hotop, H. *J. Phys. Chem. Ref. Data* **1999**, *28*, 1511.

(6) Bartmess, J. E. *Mass Spectrom. Rev.* **1989**, *8*, 297.

(7) Bartmess, J. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, July 2001; http://webbook.nist.gov.

(8) DeTuri, V. F.; Ervin, K. M. *J. Phys. Chem. A* **1999**, *103*, 6911.

(9) Shi, Y.; Ervin, K. M. *Chem. Phys. Lett.* **2000**, *318*, 149.

(10) Rodgers, M. T.; Armentrout, P. B. *J. Chem. Phys.* **1998**, *109*, 1787.

(11) Rodgers, M. T.; Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.* **1997**, *106*, 4499.

(12) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(13) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590.

(14) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764. (Supporting Information at http://chemistry.anl.gov/compmat/comptherm.htm).

(15) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

(16) Morley, G. P.; Lambert, I. R.; Mordaunt, D. H.; Wilson, S. H. S.; Ashfold, M. N. R.; Dixon, R. N.; Western, C. M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3865.

(17) Berkowitz, J.; Ruscic, B. In *Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters*; Ng, C. Y., Ed.; World Scientific: Singapore, 1991; p 1.

(18) Ruscic, B.; Litorja, M.; Asher, R. L. *J. Phys. Chem. A* **1999**, *103*, 8625. Erratum; **2000**, *104*, 8600.

(19) Ruscic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. *J. Phys. Chem. A* **2001**, *105*, 1.

(20) Martin, J. D. D.; Hepburn, J. W. *J. Chem. Phys.* **1998**, *109*, 8139.

(21) Shiell, R. C.; Hu, X. K.; Hu, Q. J.; Hepburn, J. W. *J. Phys. Chem. A* **2000**, *104*, 4339.

(22) Shiell, R. C.; Hu, X.; Hu, Q. J.; Hepburn, J. W. *Faraday Discuss.* **2000**, *115*, 331.

(23) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere Publishing Corporation: New York, 1989; Vol. 1 (Elements O, H (D, T), F, Cl, Br, I, He, Ne, Ar, Kr, Xe, Rn, S, N, P and Their Compounds), Parts 1−2.

(24) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere: New York, 1991; Vol. 2 (Elements C, Si, Ge, Sn, Pb, and Their Compounds), Parts 1−2.

(25) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.-Y.; Liu, J.; Chen, W.; Cshwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727.

(26) Harich, S. A.; Hwang, D. W. H.; Yang, X.; Lin, J. M.; Yang, X.; Dixon, R. N. *J. Chem. Phys.* **2000**, *113*, 10073.

(27) Mohr, P. J.; Taylor, B. N. *J. Phys. Chem. Ref. Data* **1999**, *28*, 1713. (http://physics.nist.gov/cuu/Constants/).

(28) Taylor, B. N.; Kuyatt, C. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; National Institute of Standards and Technology: Washington, DC, 1994. (http://physics.nist.gov/Document/tn1297.pdf).

(29) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

(30) Wickham-Jones, C. T.; Ervin, K. M.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 2762.

(31) Mordaunt, D. H.; Ashfold, M. N. R.; Dixon, R. N. *J. Chem. Phys.* **1996**, *104*, 6460.

(32) Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4319.

(33) Song, Y.; Qian, X.-M.; Lau, K.-C.; Ng, C. Y.; Liu, J.; Chen, W. *J. Chem. Phys.* **2001**, *115*, 2582.

(34) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989. (http://www.codata.org/codata/databases/key1.html).

(35) Lykke, K. R.; Murray, K. K.; Lineberger, W. C. *Phys. Rev. A* **1991**, *43*, 6104.

(36) Chuang, M.-C.; Foltz, M. F.; Moore, C. B. *J. Chem. Phys.* **1987**, *87*, 3855.

(37) Terentis, A. C.; Kable, S. H. *Chem. Phys. Lett.* **1996**, *258*, 626.

(38) Becerra, R.; Carpenter, I. W.; Walsh, R. *J. Phys. Chem. A* **1997**, *101*, 4185.

(39) Murray, K. K.; Miller, T. M.; Leopold, D. G.; Lineberger, W. C. *J. Chem. Phys.* **1986**, *84*, 2520.

(40) Smith, J. R.; Kim, J. B.; Lineberger, W. C. *Phys. Rev. A* **1997**, *55*, 2036.

(41) Wodtke, A. M.; Lee, Y. T. *J. Phys. Chem.* **1985**, *89*, 4744.

(42) Wu, C. H.; Singh, H. J.; Kern, R. D. *Int. J. Chem. Kinet.* **1987**, *19*, 975.

(43) Chen, Y.; Jonas, D. M.; Hamilton, C. E.; Green, P. G.; Kinsey, J. L.; Field, R. W. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 329.

(44) Segall, J.; Lavi, R.; Wen, Y.; Wittig, C. *J. Phys. Chem.* **1989**, *93*, 7287.

(45) Baldwin, D. P.; Buntine, M. A.; Chandler, D. W. *J. Chem. Phys.* **1990**, *93*, 6578.

(46) Balko, B. A.; Zhang, J.; Lee, Y. T. *J. Chem. Phys.* **1991**, *94*, 7958.

(47) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1990**, *93*, 5586.

(48) Segall, J.; Wen, Y.; Singer, R.; Wittig, C. *J. Phys. Chem.* **1991**, *95*, 8078.

(49) Mordaunt, D. H.; Ashfold, M. N. R. *J. Chem. Phys.* **1994**, *101*, 2630.

(50) Ervin, K. M.; Lineberger, W. C. *J. Phys. Chem.* **1991**, *95*, 1167.

(51) Taylor, T. R.; Xu, C.; Neumark, D. M. *J. Chem. Phys.* **1998**, *108*, 10018.

(52) Zemke, W. T.; Stwalley, W. C.; Coxon, J. A.; Hajigeorgiou, P. G. *Chem. Phys. Lett.* **1991**, *177*, 412.

(53) Blondel, C.; Cacciani, P.; Delsart, C.; Trainham, R. *Phys. Rev. A* **1989**, *40*, 3698.

(54) Blondel, C. *Phys. Scr.* **1995**, *T58*, 31.

(55) Hepburn, J. W.; Martin, J. D. D. *Faraday Discuss.* **2000**, *115*, 416.

(56) Yencha, A. J.; Lopes, M. C. A.; King, G. C.; Hochlaf, M.; Song, Y.; Ng, C.-Y. *Faraday Discuss.* **2000**, *115*, 355.

(57) Wilson, S. H. S.; Howe, J. D.; Ashfold, M. N. R. *Mol. Phys.* **1996**, *88*, 841.

(58) Breyer, F.; Frey, P.; Hotop, H. *Z. Physik A* **1981**, *300*, 7.

(59) Larson, D. J.; Edge, C. J.; Elmquist, R. E.; Mansour, N. B.; Trainham, R. *Phys. Scr. T* **1988**, *22*, 183.

(60) Bradforth, S.; Kim, E.; Arnold, D.; Neumark, D. *J. Chem. Phys.* **1993**, *98*, 800.

(61) Cook, P. A.; Langford, S. R.; Ashfold, M. N. R.; Dixon, R. N. *J. Chem. Phys.* **2000**, *113*, 994.

(62) Berkowitz, J.; Chupka, W. A.; Walter, T. A. *J. Chem. Phys.* **1969**, *50*, 1497.

(63) Berzinsh, U.; Gustafsson, M.; Hanstorp, D.; Klinkmüller, A.; Ljungblad, U.; Mårtensson-Pendrill, A.-M. *Phys. Rev. A* **1995**, *51*, 231.

(64) Hanstorp, D.; Gustafsson, M. *J. Phys. B: At. Mol. Opt. Phys.* **1992**, *25*, 1773.

(65) Bartmess, J. E.; Pittman, J. L.; Aeschleman, J. A.; Deakyne, C. A. *Int. J. Mass Spectrom.* **2000**, *196*, 215.

(66) Irikura, K. K. In *Energetics of Stable Molecules and Reactive Intermediates*; Minas da Piedada, M. E., Ed.; Kluwer: Dordrecht, , 1999; p 353.

(67) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517.

(68) MacKay, G. J.; Hemsworth, R. S.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1624.

(69) Karpas, Z.; Klein, F. S. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 65.

(70) Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153.

(71) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(72) Bohme, D. K.; MacKay, G. I.; Schiff, H. I.; Hemsworth, R. S. *J. Chem. Phys.* **1974**, *61*, 2175.

(73) Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153.

(74) Bierbaum, V. M.; Schmidt, R. J.; DePuy, C. H.; Mead, R. H.; Schulz, P. A.; Lineberger, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6262.

(75) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1.

(76) Rempala, K.; Ervin, K. M. *J. Chem. Phys.* **2000**, *112*, 4579.

(77) Trainham, R.; Fletcher, G. D.; Larson, D. J. *J. Phys. B: At. Mol. Phys.* **1987**, *20*, *L777*.

(78) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

(79) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.

(80) Bohme, D. K.; Hemsworth, R. S.; Rundle, H. W. *J. Chem. Phys.* **1973**, *59*, 77.

(81) Betowski, D.; Mackay, G.; Payzant, J.; Bohme, D. *Can. J. Chem.* **1975**, *53*, 2365.

(82) Ramond, T. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C. *J. Chem. Phys.* **2000**, *112*, 1158.

(83) Osborn, D. L.; Leahy, D. J.; Kim, E. H.; de Beer, E.; Neumark, D. M. *Chem. Phys. Lett.* **1998**, *292*, 651.

(84) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(85) Osborn, D. L.; Leahy, D. J.; Ross, E. M.; Neumark, D. M. *Chem. Phys. Lett.* **1995**, *235*, 484.

(86) Xu, K.; Amaral, G.; Zhang, J. *J. Chem. Phys.* **1999**, *111*, 6271.

(87) Russell, J. J.; Senkan, S. M.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1989**, *93*, 5184.

(88) Kaiser, E. W.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 4111.

(89) Pilgrim, J. S.; Taatjes, C. A. *J. Phys. Chem. A* **1997**, *101*, 4172. Erratum; **1997**, *101*, 8741.

(90) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem.* **1996**, *100*, 16899.

(91) Parmar, S. S.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 2652.

(92) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.

(93) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series; Thermodynamics Research Center: College Station, TX, 1994; Vol. 1.

(94) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(95) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.

(96) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **2000**, *498*, 123.

(97) Smith, B. J.; Pople, J. H.; Curtiss, L. A.; Radom, L. *Aust. J. Chem.* **1992**, *45*, 285.

(98) Pokon, E. K.; Liptak, M. D.; Feldgus, S.; Shields, G. C. *J. Phys. Chem. A* **2001**, *105*, 10483.

(99) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(100) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(101) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6792.

(102) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(103) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(104) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(105) Burk, P.; Koppel, I. A.; Koppel, I.; Leito, I.; Travnikova, O. *Chem. Phys. Lett.* **2000**, *323*, 482.

(106) Merrill, G. N.; Kass, S. R. *J. Phys. Chem.* **1996**, *100*, 17465.